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13. ABSTRACT (Maximum 200 words) Towards the high performance nonlinear optical polymers, a novel class of side-chain NLO polyquinolines had been designed and the first side-chain NLO polyquinoline had also been synthesized in this period. The starting materials of 4,4'-diamino-3,3'-dibenzoyl-diphenyl ether and 2,4-diacetyl-[2-(N-ethyl-anilino)ethoxy]benzene for the side-chain polyquinoline had been synthesized and fully characterized. A crosslinkable maleimides terminated NLO oligomers and polymers via curing of aromatic diamines had been designed and the starting material had been prepared.			
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PROGRESS REPORT #1

15 August, 1994 - 14 October, 1994

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PROGRESS REPORT #1

1. OBJECTIVES OF THE RESEARCH EFFECT

The main objective of the research activity of this program is to design and synthesize highly efficient NLO polymers possessing high E-O coefficient (r_{33}), good processibility, and high temperature alignment stability of the poled NLO chromophores. The general approaches include the incorporation of highly efficient and thermally stable heteroaromatic NLO chromophores in high performance polyimides and polyquinolines, to achieve the following properties:

- Large E-O coefficient ($r_{33} > 20$ pm/V at 1.3 μ m).
- High temperature alignment stability of the poled polymers (short-term stability at 300°C for 0.5 h and long-term stability at 100°C for over 1000 h).
- Low optical loss (suitable for device design).
- Reproducibility (can be supplied to end-users).

2. STATUS OF THE RESEARCH EFFORT

1) Background of the Research

Active electro-optical polymer modulators and switches have been studied extensively by many leading research groups using a variety of aromatic nonlinear optical chromophores in polymer matrices. However, typical E-O polymer systems that are reported in the literature are not compatible with required high temperature processing conditions for integrated optic devices. In many cases, the chromophores cannot survive the vigorous conditions required to process suitable polymer matrices. In addition, most useful devices will require multilayer processing which imposes additional severe constraints on the properties of the materials.

Among the NLO-active polymer materials, the guest/host NLO chromophore-polymer systems are the most extensively investigated. Although the results reported with these guest/host

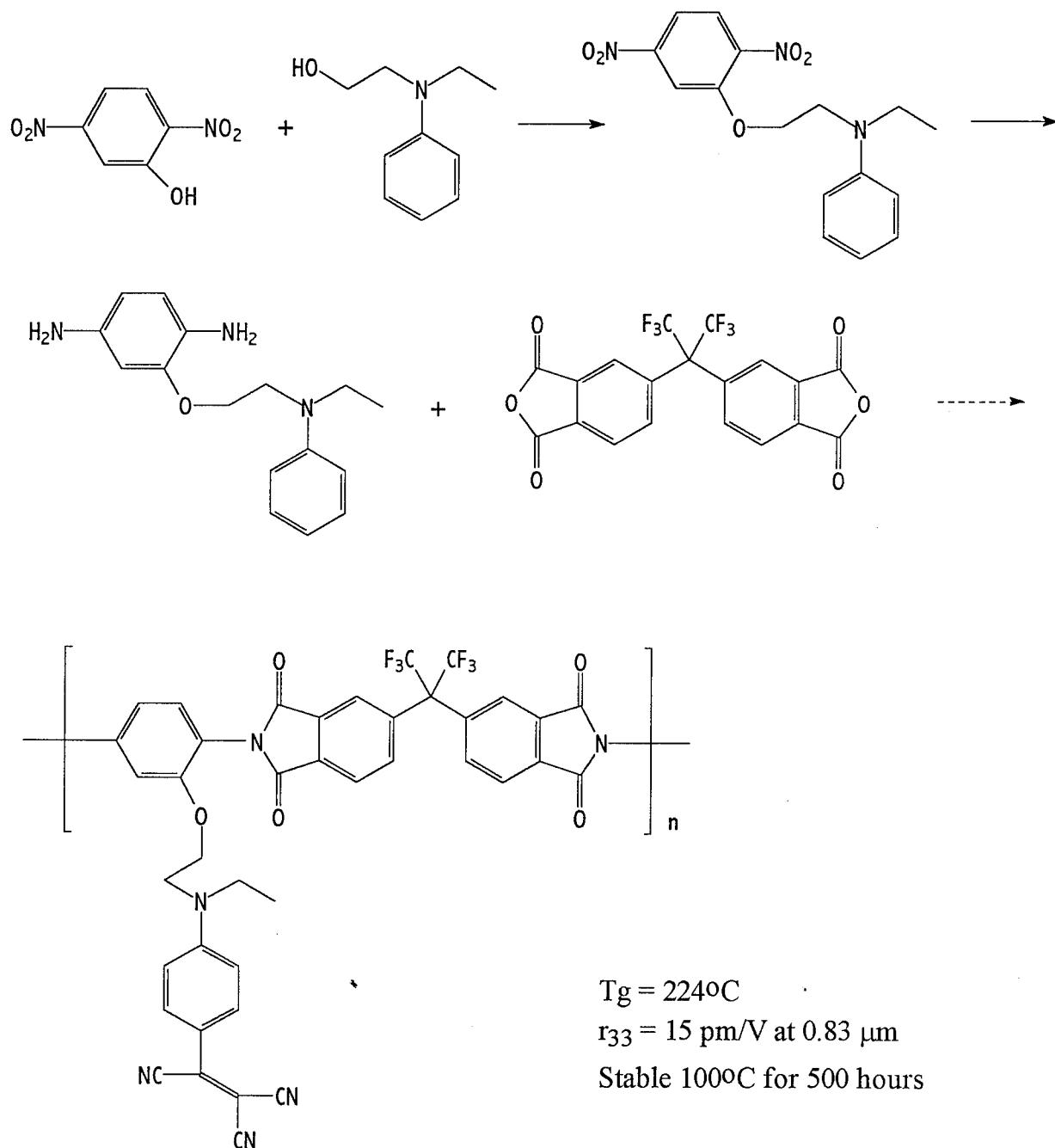
type NLO materials are quite encouraging, several deficiencies do exist, such as the limitation of effective chromophore loading due to incompatibility between the polymer host and the chromophores guest, the sublimation and diffusion of low molecular weight chromophores at prolonged high working temperatures, the plasticization of the polymer materials by chromophores, and the extraction of dye molecules by organic solvents encountered in building multilayer devices with the solution casting method. To address these problems, we have been focused on incorporation of high performance heteroaromatic NLO chromophores into highly thermally-stable, optical quality polymer systems, such as polyquinolines and polyimides, via covalent bonding or crosslinking techniques. The promising initial program impacts include:

a) EniChem's earlier results demonstrate that the use of heteroaromatics as conjugating moieties strongly enhances the molecular hyperpolarizability ($\beta\mu$) of the charge transfer compounds. At present, EniChem's researchers have made numerous classes of molecules with excellent optical nonlinearity ($\beta\mu$ value as high as 10000×10^{-48} esu). The broad range of absorption spectra and very high nonlinearity achieved by employing heteroaromatics as conjugating moieties coupled with various efficient electron donors and acceptors clearly provides a vast array of potential molecules.

Having achieved a major success in primary nonlinear optical properties, EniChem's scientists have focused their research on obtaining suitable secondary properties. A unique approach was developed to enhance thermal and photochemical stability of chromophores without sacrificing optical nonlinearity. Functionalized heteroaromatic conjugated compounds without π -bridges, such as fused-ringed or single-ring heteroaromatics, possess high thermal stability ($>300^\circ\text{C}$) and are photochemically stable to visible light. The achievement of intrinsic thermal and photochemical stability, however, is not sufficient to ensure high temperature stability in a polymer matrix. Therefore, the covalent incorporation of chromophores into a polymer matrix has become crucially important.

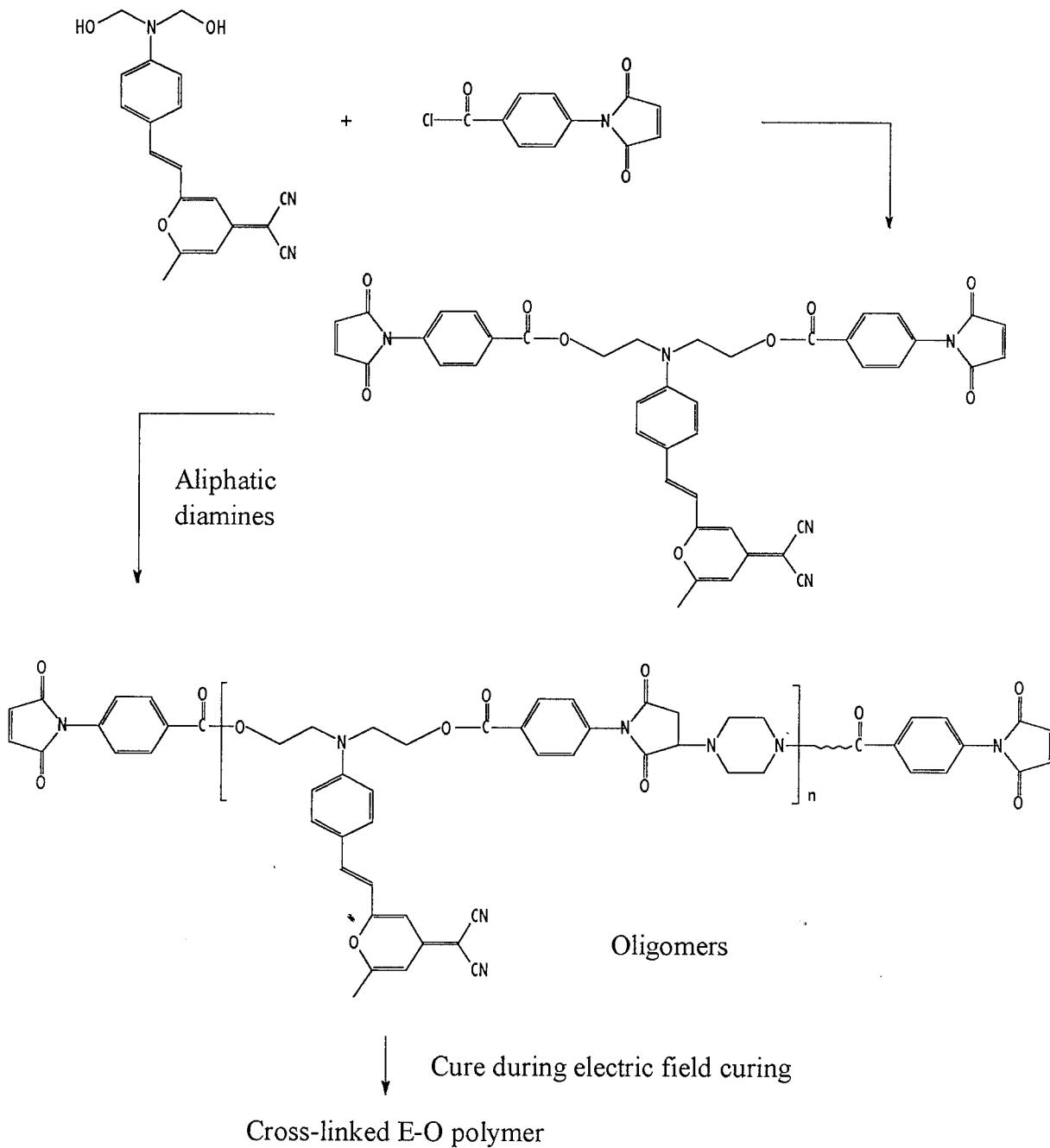
b) A new synthetic approach for side-chain *aromatic* polyimides had been developed as shown in scheme 1.

SCHEME 1: New Synthetic Approach for Aromatic Side-Chain Aromatic Polyimides

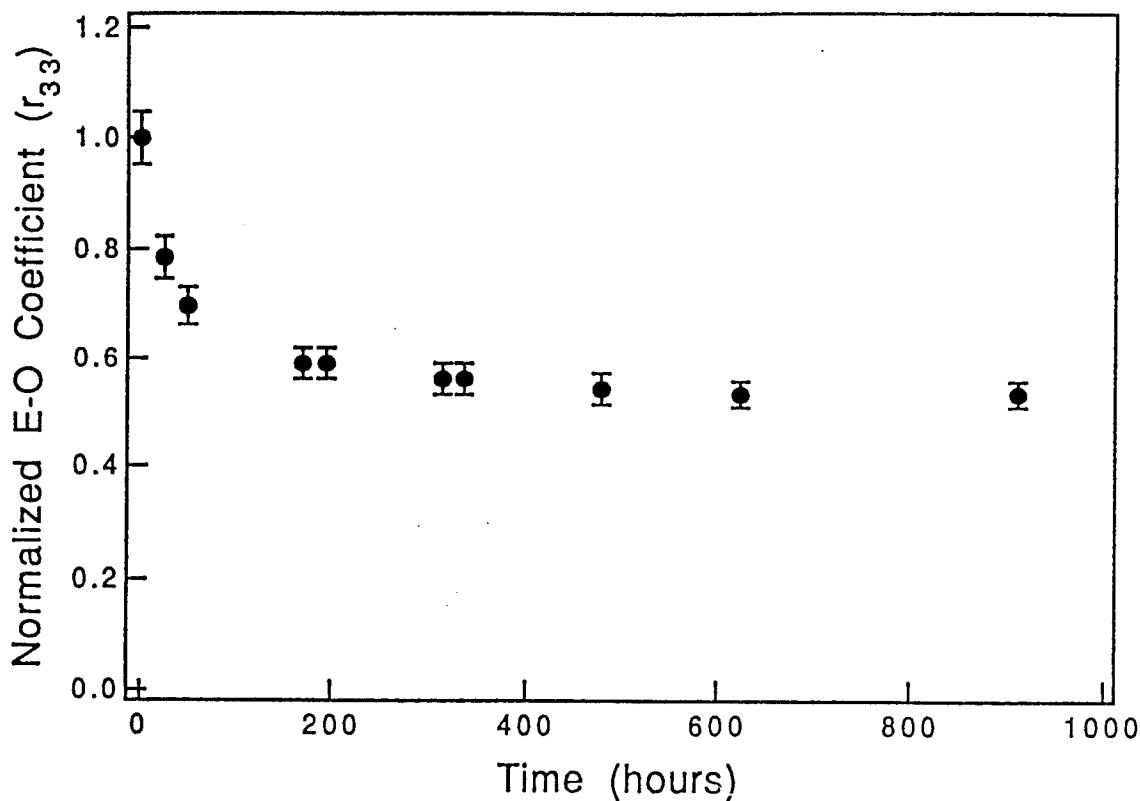


The NLO side-chain aromatic polyimide system had glass-transition temperature $T_g = 224^\circ\text{C}$, E-O coefficient $r_{33} = 15 \text{ pm/V}$ at $0.83 \mu\text{m}$, and stability at 100°C for 500 h.

c) Maleimide terminated oligomers and polymers via curing of *aliphatic* diamines had the properties of $r_{33} = 12 \text{ pm/V}$ at $1.3 \mu\text{m}$, and very good poled thermal stability at 100°C (Scheme 2):

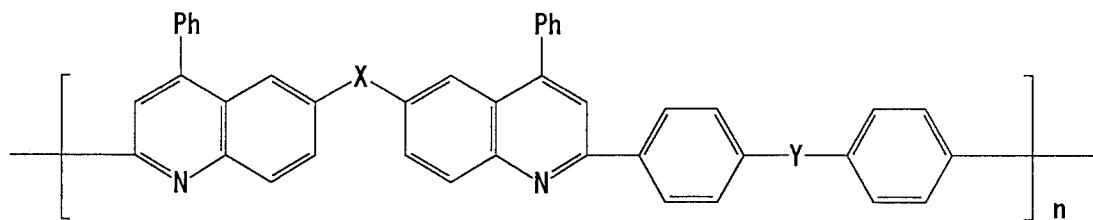


d) A guest/host system of polyquinoline NLO chromophore (20 wt %) was developed with a $T_g = 295^\circ\text{C}$ and an electrooptic coefficient $r_{33} = 45 \text{ pm/V}$ measured at $1.3 \mu\text{m}$ with a poling field of 0.8 MV/cm . The r_{33} retained a value of 25 pm/V after 100°C for 1000 h . This r_{33} value is the highest reported to date to our knowledge.



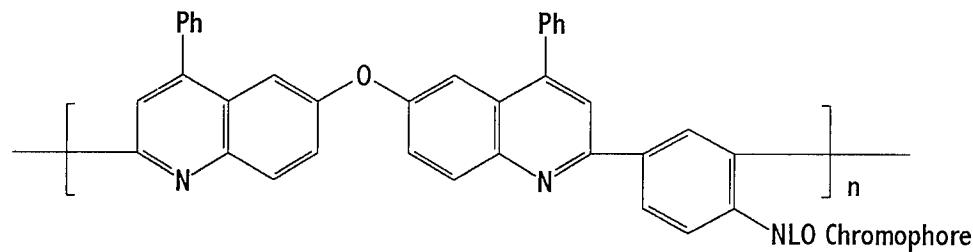
2) Status of the Research

a) Polyquinolines, which were discovered by Stille and his co-workers, represent a class of high temperature and thermo-oxidative stable polymers made by the condensation reaction of ketomethylene compounds and *ortho*-amino ketones. The wide variety of monomers and the ability of the quinoline-forming reaction to generate high molecular weight polymers under relatively mild conditions allows the synthesis of a large series of polyquinolines.

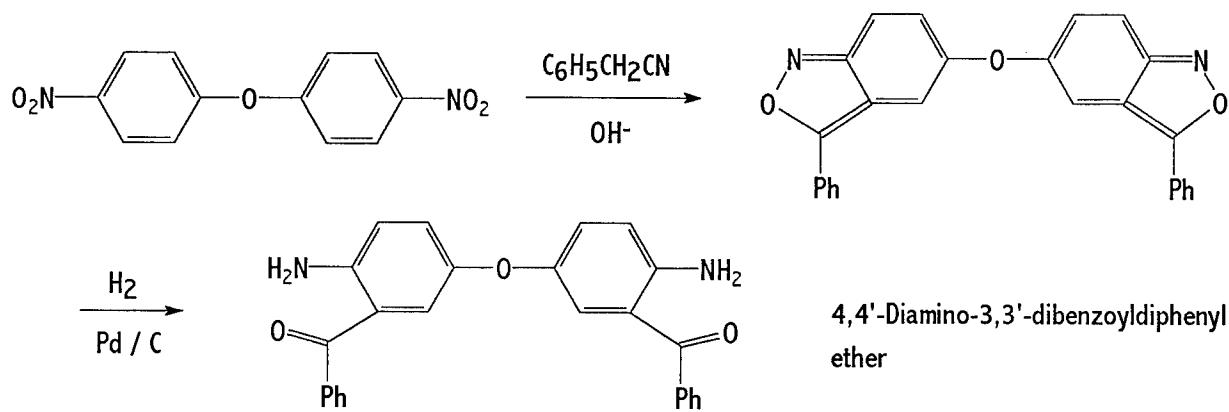


The additional promising properties of polyquinolines for their application in NLO materials include very low dielectric constant, very low moisture uptake, stability in solution at room temperature, very high glass-transition temperature (250-380°C) and thermal stability (>450°C), low shrinkage, and compatibility with plasma or reactive ion etching.

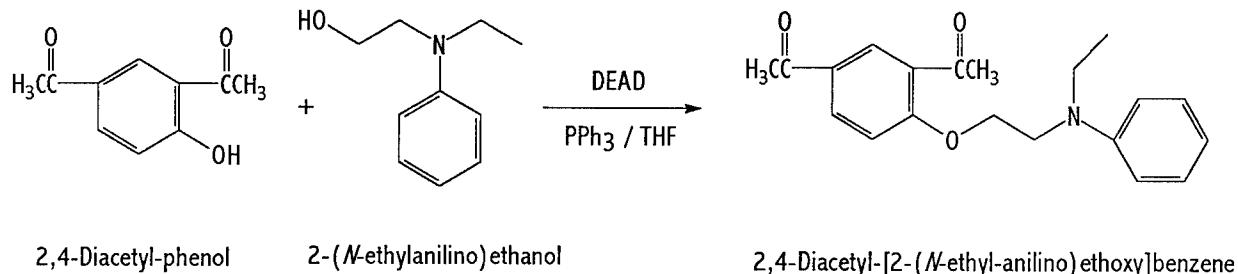
Our research of this period focused on the side-chain polyquinoline system based on the encouraging results of the guest/host NLO polyquinoline system. The guest/host NLO polyquinoline system suffered plasticizing and sublimation problems of the chromophores, although the system exhibited an excellent E-O property. These problems of the guest/host polyquinoline system are expected to be solved by connecting a chromophore onto the polyquinoline backbone through covalent bonding. Thus, a novel class of side-chain NLO chromophore polyquinolines had been designed by us:



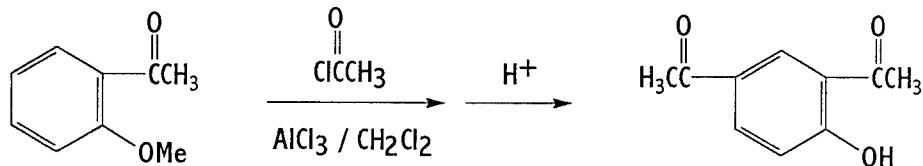
The starting materials of 4,4'-diamino-3,3'-dibenzoyldiphenyl ether and 2,4-diacetyl-[2-(*N*-ethylanilino)ethoxy]benzene had been synthesized and fully characterized:



The novel starting material 2,4-diacetyl-[2-(*N*-ethylanilino)ethoxy]benzene was designed and synthesized by us. The compound was prepared by a Mitsunobu reaction between 2-(*N*-ethylanilino)ethanol and 2,4-diacetyl-phenol.

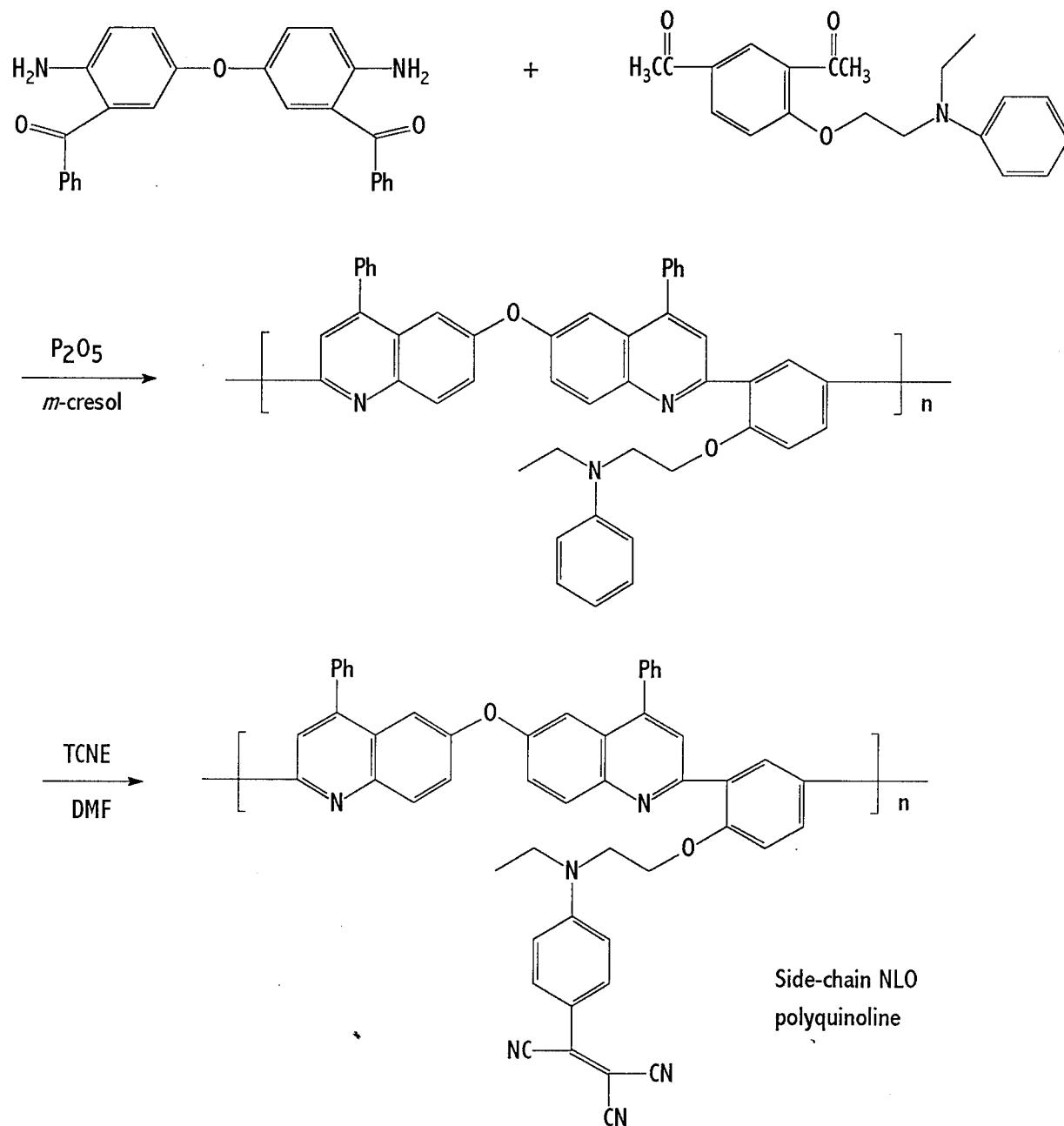


2,4-Diacetyl-phenol was prepared from 2'-methoxy-acetophenone by a novel reaction which combined acetylation and deprotection in one step:



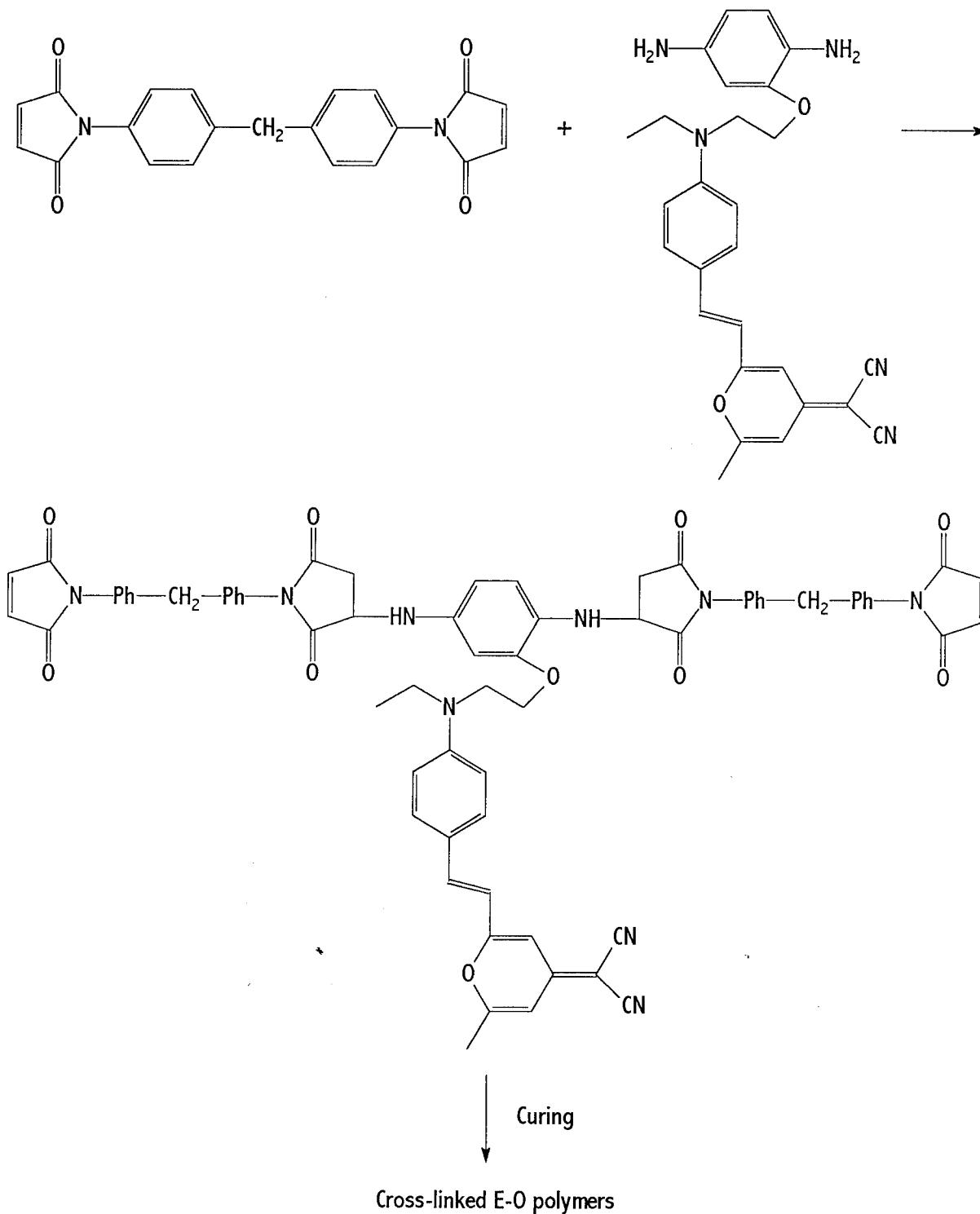
In this period, the first side-chain chromophore NLO polyquinoline was also synthesized by us as shown in the following scheme:

SCHEME 3. Synthesis of Side-Chain NLO Polyquinoline



The polyquinoline was prepared by the condensation of *ortho*-amino-ketone compound and diacetyl compound. The side-chain NLO chromophore polyquinoline was further prepared by the post tricyanization of polyquinoline. The detail analysis and measurement data of the side-chain NLO polyquinoline system will be presented in next progress report.

b) A crosslinkable maleimide terminated NLO oligomer and polymer via curing of aromatic diamine was designed and the starting material was prepared:



The detail results for this polymer will be presented in the following report.

3. PUBLICATIONS IN TECHNICAL JOURNALS

- 1) "High Temperature Poled Side-Chain Polyimides for Electro-optical Applications", A. K.-Y. Jen, Y. M. Cai, K. J. Drost, Y. J. Liu, V. P. Rao, T.-A. Chen, R. M. Mininni and J. T. Kenney, *Polymeric Materials: Science and Engineering* (1995), Preprint in press.
- 2) "The Development of Highly Active, Thermally Stable Chromophores and Polymers for Electro-Optical Applications", A. K.-Y. Jen, V. P. Rao, Y. M. Cai, K. J. Drost, Y. J. Liu, and J. T. Kenney, Extended abstract, P. 13, 5th International Conference on Polyimide, 1994.

5. PAPERS PRESENTED AT MEETINGS, CONFERENCES, SEMINARS, ETC.

- 1) "The Development of Highly Active, Thermally Stable Chromophores and Polymers for Electro-Optical Applications", A. K.-Y. Jen, V. P. Rao, Y. M. Cai, K. J. Drost, Y. J. Liu and J. T. Kenney, 5th International Conference on Polyimides, Ellenville, New York, November 2, 1994.